Alternative derivation of the freezing point depression formula for binary aqueous solutions (class notes)

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January 9, 2026

Introduction

There are at least two ways to arrive at the function for the liquidus temperature as a function of activity of species at solid-liquid equilibrium. The first is using the Gibbs-Helmholtz relationship, which is the most commonly found approach. The second is to use the equality of chemical potentials of species at equilibrium without direct use of the Gibbs-Helmholtz relation. Although likely present in the literature, a detailed account of the second method is not easy to find. As such this approach is the subject of the present work.

Freezing point depression

Freezing point depression is a very well known phenomenon which occurs when a solvent's freezing point is lowered through addition of a solute which forms a liquid solution with the solvent. This is for example the motivation for using road salt, such as $CaCl_2$, which, when in solution with water, can significantly reduce the freezing temperature. The equilibrium in question is the following equilibrium:

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)} \tag{1}$$

The equilibrium temperature T^{fus} between ice and the liquid phase (ice + L) and the liquid phase (L) shown in Figure 1 reduces as the concentration of $CaCl_2$ is increased. The change in freezing point depends on the concentration of salt, and more precisely, on its thermodynamic activity. The derivation that follows assumes a basic knowledge of thermodynamics, including an understanding of the quantity of chemical potential of a species in a given phase μ_i^{phase}.

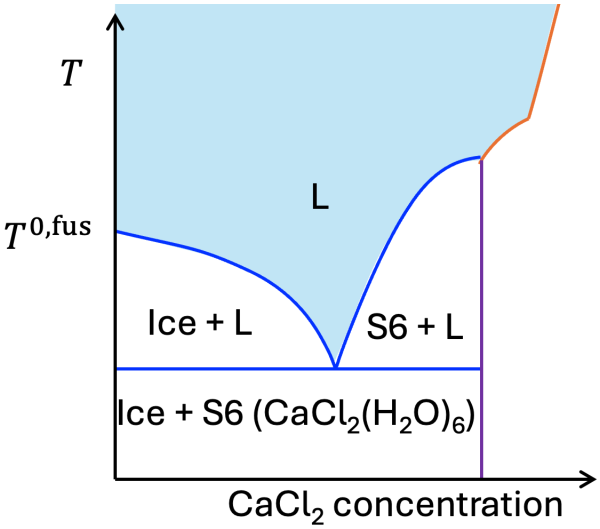

Figure 1: Partial phase diagram of $CaCl_2$ in H_2O adapted from Conde.[1]

Isochemical potential condition

In order to describe solid-liquid equilibrium, we will use the example of freezing point depression of water when in a liquid solution such as when $CaCl_2$ is added to H_2O. At solid-liquid equilibrium for ice freezing out from a solution, the chemical potential of water is the same in both phases:

$$\mu^{s}_{\mathrm{H2O}} = \mu^{l}_{\mathrm{H2O}} \tag{2}$$

The above equation can be generalized for other phase equilibria conditions as well. At the standard state at 273.15 K and 1 atmosphere of pressure, the following equality is established:

$$\mu^{0,l}_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}}) - \mu^{0,s}_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}}) = \Delta H^{0,\mathrm{fus}}(T = T^{0,\mathrm{fus}}) - T^{0,\mathrm{fus}}\Delta S^{0,\mathrm{fus}}(T = T^{0,\mathrm{fus}}) \tag{3}$$

Since at equilibrium, $\mu^{0,s}_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}}) - \mu^{0,l}_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}}) = 0$, this allows writing the change in entropy of fusion at that temperature as:

$$\Delta S^{0,\mathrm{fus}}(T = T^{0,\mathrm{fus}}) = \frac{\Delta H^{0,\mathrm{fus}}(T = T^{0,\mathrm{fus}})}{T^{0,\mathrm{fus}}} \tag{4}$$

At solid-liquid equilibrium, the chemical potentials of water in the liquid state will not be at the standard state once a solute is added, but the solid will be if we assume no solute dissolves appreciably in ice. Accordingly, the difference of water's chemical potential in both phases can be written as:

$$\mu^{l}_{\mathrm{H2O}}(T) - \mu^{s}_{\mathrm{H2O}}(T) = \mu^{0,l}_{\mathrm{H2O}}(T) + RT\ln a_{\mathrm{H2O}}(T) - \mu^{0,s}_{\mathrm{H2O}}(T) \tag{5}$$

At the solid-liquid equilibrium, the chemical potentials in the solid phase and liquid phase are the same, yielding the following equality:

$$RT\ln a_{\mathrm{H2O}}(T^{\mathrm{fus}}) = \mu^{0,s}_{\mathrm{H2O}}(T^{\mathrm{fus}}) - \mu^{0,l}_{\mathrm{H2O}}(T^{\mathrm{fus}}) \tag{6}$$

Thus, the activity of water in the liquid solution is a function of the change in chemical potentials in the standard state of water at the equilibrium temperature. However, the thermodynamic properties of the entropy change at standard state and enthalpy change at standard state have to be adjusted at the right temperature. This can be achieved via the following relations:

$$\Delta S^{0,\mathrm{fus}}(T = T^{\mathrm{fus}}) = \Delta S^{0,\mathrm{fus}}(T = T^{0,\mathrm{fus}}) + \int_{T^{0,\mathrm{fus}}}^{T^{\mathrm{fus}}} \frac{\Delta C_P(T)}{T} dT \tag{7}$$

$$\Delta H^{0,\mathrm{fus}}(T = T^{\mathrm{fus}}) = \Delta H^{0,\mathrm{fus}}(T = T^{0,\mathrm{fus}}) + \int_{T^{0,\mathrm{fus}}}^{T^{\mathrm{fus}}} \Delta C_P(T) dT \tag{8}$$

Now we can solve for the activity of water at the fusion temperature, which in the case of freezing point depression will be lower than the standard state fusion temperature $T^{0,\mathrm{fus}}$.

$$\begin{aligned} & - RT^{\mathrm{fus}}\ln a_{\mathrm{H2O}}(T^{\mathrm{fus}}) = \\ & \Delta H^{0,\mathrm{fus}}(T^{0,\mathrm{fus}}) + \int_{T^{0,\mathrm{fus}}}^{T^{\mathrm{fus}}} \Delta C_P(T) dT - T^{\mathrm{fus}}(\Delta S^{0,\mathrm{fus}}(T^{0,\mathrm{fus}}) + \int_{T^{0,\mathrm{fus}}}^{T^{\mathrm{fus}}} \frac{\Delta C_P(T)}{T} dT) \end{aligned}$$

The above equation is exact. The left hand side is an expression for the activity of water in the solution at the equilibrium temperature. The right hand side is a collection of terms which depend on the standard state thermodynamic properties of the water undergoing phase change. The entropy change term may be substituted by an enthalpy change term:

$$
\begin{aligned}
&-RT^{\mathrm{fus}}\ln a_{\mathrm{H2O}}(T^{\mathrm{fus}}) = \\
&\Delta H^{0,\mathrm{fus}}(T^{0,\mathrm{fus}}) + \int_{T^{0,\mathrm{fus}}}^{T^{\mathrm{fus}}} \Delta C_P(T)dT - T^{\mathrm{fus}}\left(\frac{\Delta H^{0,\mathrm{fus}}(T^{0,\mathrm{fus}})}{T^{0,\mathrm{fus}}} + \int_{T^{0,\mathrm{fus}}}^{T^{\mathrm{fus}}} \frac{\Delta C_P(T)}{T}dT\right)
\end{aligned}
$$

This expression is attractive since the enthalpy of fusion of the neat solvent, here water, is well known. Moreover, the heat capacity change upon fusion is for the neat solvent only — not a function of the solution composition. However, in many circumstances the relevant quantity is the activity of the solvent at a temperature other than the solid-liquid equilibrium temperature of the solution. If we can assume the activity has no temperature dependence between the neat solvent fusion temperature and the new fusion temperature, and we can neglect the heat capacity change of the neat solvent upon fusion ($\Delta C_P \simeq 0$), we have the following equation:

$$
\begin{aligned}
&-\ln(a_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}}) \simeq -\ln(a_{\mathrm{H2O}}(T = T^{\mathrm{fus}})) = \\
&-\frac{1}{RT^{\mathrm{fus}}}\left(\Delta H^{0,\mathrm{fus}}(T^{0,\mathrm{fus}}) - T^{\mathrm{fus}}(\frac{\Delta H^{0,\mathrm{fus}}(T^{0,\mathrm{fus}})}{T^{0,\mathrm{fus}}})\right)
\end{aligned}
$$

Rearranging the same terms we obtain:

$$
\ln(a_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}}) \simeq \ln(a_{\mathrm{H2O}}(T = T^{\mathrm{fus}})) = \frac{-\Delta H^{0,fus}}{RT^{\mathrm{fus}}}\left(\frac{T^{0,\mathrm{fus}} - T^{\mathrm{fus}}}{T^{0,\mathrm{fus}}T^{\mathrm{fus}}}\right) \tag{9}
$$

However, an exact relation between of $\ln(a_{\mathrm{H2O}}(T = T^{0,\mathrm{fus}})$ and the liquidus temperature of the solution requires treatment of the water activity temperature dependence. The physical chemistry underlying the temperature dependence of activity is quite involved and may not easily be written with a closed form expression. However, with a phenomenological parameter L_1 which is a function of composition but approximated as independent of temperature, the following expression can be used:

$$R\ln(a_{\mathrm{H2O}}(T_1)) - R\ln(a_{\mathrm{H2O}}(T_2)) \simeq -L_{\mathrm{H2O}}(\frac{1}{T_2} - \frac{1}{T_1}) = -L_{\mathrm{H2O}}(\frac{T_1 - T_2}{T_1 T_2}) \tag{10}$$

In certain circumstances, L_{H2O}, can be fitted to experimental data of activities using the above expression, which becomes increasingly accurate as the difference between T_1 and T_2 decreases. The motivation for this expression will be detailed in the following subsection. Certain cases may require terms beyond L_{H2O} to better account for the temperature dependence of activities. Such terms include for example the relative partial molal heat capacity J_1. Figure 1 shows reported values[2] of L_{H2O} at 25 °C. Applying the above formula for $T^{0,\mathrm{fus}}$ and T^{fus}:

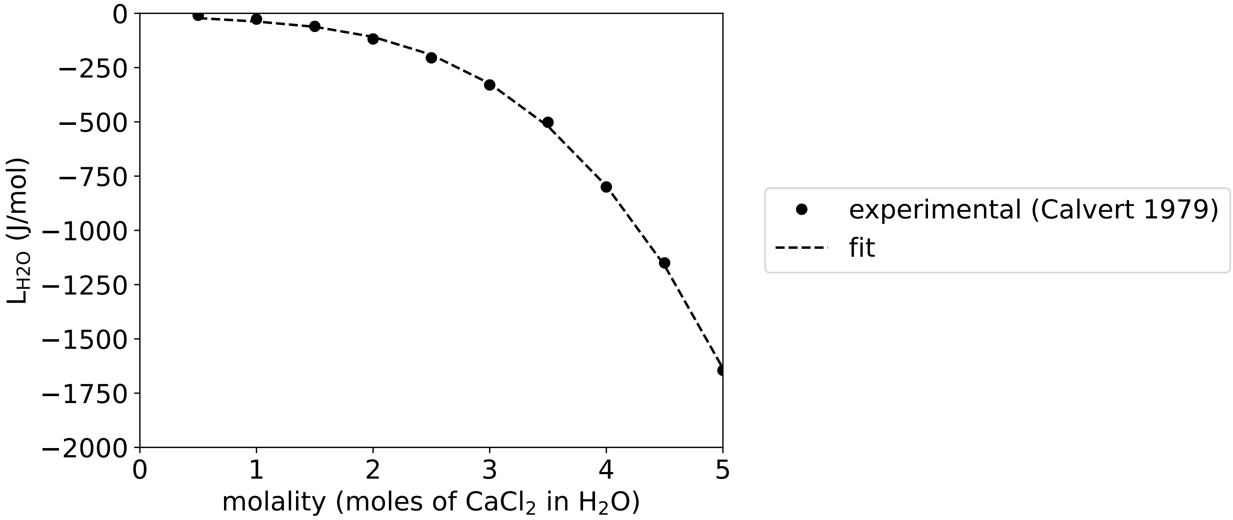

Figure 2: L_{H2O} at 25°C from reported values[2] (circles) and fit with a polynomial in the present work (dashed lines).

$$R\ln(a_{\mathrm{H2O}}(T^{0,\mathrm{fus}})) \simeq R\ln(a_{\mathrm{H2O}}(T^{\mathrm{fus}})) - L_{\mathrm{H2O}}\left(\frac{T^{0,\mathrm{fus}} - T^{\mathrm{fus}}}{T^{0,\mathrm{fus}} T^{\mathrm{fus}}}\right) \tag{11}$$

Accordingly, we can now relate the activity of water at the neat solvent fusion temperature to the new fusion (or freezing) temperature:[3]

$$R\ln(a_{\mathrm{H2O}}(T^{0,\mathrm{fus}})) \simeq -(\Delta H^{\mathrm{fus}} + L_{\mathrm{H2O}})(\frac{T^{0,\mathrm{fus}} - T^{\mathrm{fus}}}{T^{0,\mathrm{fus}} T^{\mathrm{fus}}}) \tag{12}$$

If heat capacity terms are important, the above expression can include additional terms. For example, Lewis et al.[3] consider the case where the heat capacity change upon fusion of the neat solvent is a linear function of temperature, and assume the relative partial molal heat capacity is a constant as a function of temperature. The latter is equivalent to considering the temperature dependence of L_{H2O}. We can compare equation 12 to 26-9 of Lewis et al.[3] for the special case where we neglect the heat capacity upon fusion and the relative partial molal heat capacity J_1 is taken to 0.

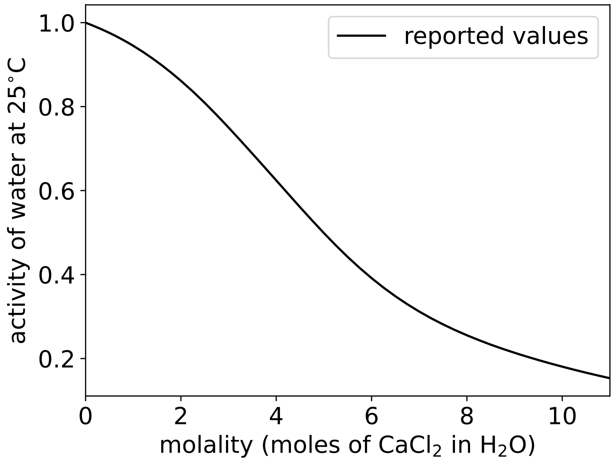

Figure 3: Activity of water at 25 °C from reported values.[4]

Figure 3 shows the reported activity of water as a function of concentration at a fixed temperature. Here, the activity of water is known and one may desire to calculate the liquidus temperature as a function of composition. The above equation can be inverted to calculate the liquidus temperature from the activity:

$$T^{\mathrm{fus}} = \frac{T^{0,\mathrm{fus}}}{1 + RT^{0,\mathrm{fus}} \ln a_{\mathrm{H2O}} \frac{1}{-(\Delta H^{\mathrm{fus}} + L_1)}} \tag{13}$$

Using the data from Figure 3 and equation 13, we can calculate the freezing point depression as a function of concentration, or equivalently, the fusion temperature as a function of concentration.

Figure 4 shows the freezing point depression of water as a function of $CaCl_2$ concentration

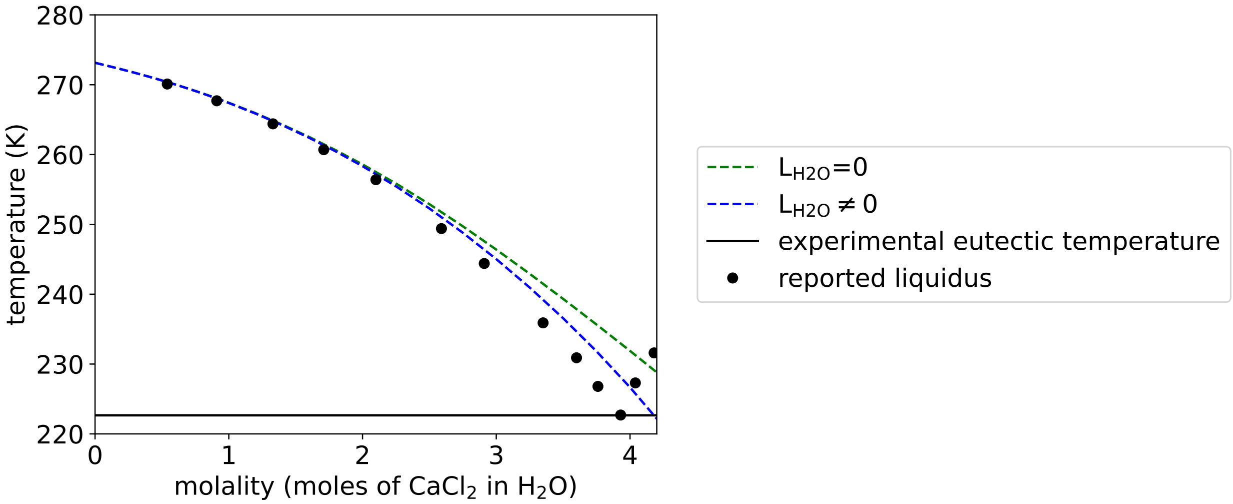

Figure 4: Solid-liquid equilibrium temperature T^{fus} as a function of CaCl_2 concentration (circles[5] and dashed lines) and reported[5] eutectic temperature.

calculated from the data shown in Figure 3 and equation 13 (dashed lines). In the case of L_{H2O}=0, the agreement with the experimental points is excellent at lower CaCl_2 concentrations, but becomes more significant as the CaCl_2 concentration increases. This is due to two factors, the neglect of heat capacity difference upon fusion (neglected in this document) and the temperature dependence of activity, which is accounted for here via the $L_{\text{H2O}} \neq 0$ case (dashed blue). Here, the agreement is closer to experimental values, showing that consideration of L_{H2O} can improve the calculation of phase equilibria temperatures. It is interesting to note that certain authors[6] suggest that accounting for the effect of L_{H2O} is more important than ΔC_P (not considered in this document), while others suggest the converse.[7] Despite not knowing the scale of importance of both these quantities on predicting freezing point depression in a universal sense, it is clear both terms can have in certain circumstances a non-negligible effect, in addition to J_1 which can also be important.

Activity dependence on temperature

The reason for choosing the above relation for the activity dependence on temperature in equation 10 is that the parameter L_{H2O} is one that in principle could be measured via specific calorimetry experiments. The Gibbs-Helmholtz relation,[3] previously avoided in this document, allows us to identify L_{H2O} as the partial relative molal enthalpy H^E_{H2O}.[6] For example:

$$R\left[\frac{\partial \ln a_{\mathrm{H2O}}}{\partial(\frac{1}{T})}\right] = H^0_{\mathrm{H2O}} - H_{\mathrm{H2O}} = H^E_{\mathrm{H2O}} \simeq L_{\mathrm{H2O}} \qquad (14)$$

Accordingly, L_{H2O} should reach 1 as the solute composition reaches 0. In addition, in this document the relative partial molal heat capacity J_1 is approximated as negligible.

Liquidus lines for hydrates and higher order equilibria

As shown in Figure 1, the freezing point decreases until the first eutectic composition, after which it can start increasing. The increase in freezing temperature with increase in salt concentration appears for different solid-liquid equilibria dictated by solid hydrates containing salt, for example $\mathrm{CaCl_2(H_2O)_6}$(solid). Analogous expressions to equation 13 can be developed for solid-liquid equilibria involving hydrates, using once again the isochemical potential condition. However, the activities of species in solution to consider will include those of the salt and solvent in the solution, and thermodynamic properties of the solid relevant to the equilibrium.[6] The motivation for this derivation arises from my proposition that the Gibbs-Helmholtz relation, although rigorous, is not necessarily intuitively applied to solid-equilibria featuring different species, or a collection of equilibria in the case of for example a eutectic point, where a liquid solution is in equilibrium with two solid phases.

References

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